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Lewis Acid Catalyzed Conversion of 5-Hydroxymethylfurfural to 1,2,4-Benzenetriol, an Overlooked Biobased Compound

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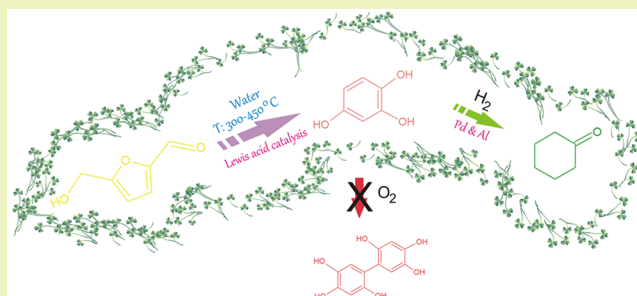
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Supporting Information

ABSTRACT: 5-Hydroxymethylfurfural (HMF) is a platform chemical that can be produced from renewable carbohydrate sources. HMF can be converted to 1,2,4-benzenetriol (BTO) which after catalytic hydrodeoxygenation provides a route to cyclohexanone and cyclohexanol. This mixture, known as KA oil, is an important feedstock for polymeric products such as nylons which use benzene as feedstock that is obtained from the BTX fraction produced in oil refineries. Therefore, the conversion of HMF to BTO provides a renewable, alternative route toward products such as nylons. However, BTO is usually considered an undesired byproduct in HMF synthesis and is only obtained in small amounts. Here, we show that Lewis acid catalysts can be utilized for the selective conversion of HMF to BTO in subsupercritical water. Overall, up to 54 mol % yield of BTO was achieved at 89% HMF conversion using ZnCl_2 . ZnCl_2 and similarly effective $\text{Zn}(\text{OTf})_2$ and $\text{Fe}(\text{OTf})_2$ are known as relatively soft Lewis acids. Other Lewis acid like $\text{Hf}(\text{OTf})_4$ and $\text{Sc}(\text{OTf})_3$ gave increased selectivity toward levulinic acid (up to 33 mol %) instead of BTO, a well-known HMF derivative typically obtained by acid catalysis. Catalytic hydrodeoxygenation of BTO toward cyclohexanone in water was achieved in up to 45% yield using 5 wt % Pd on Al_2O_3 combined with AlCl_3 or $\text{Al}(\text{OTf})_3$ as catalysts. Additionally, a mild selective oxygen induced dimerization pathway of BTO to 2,2',4,4',5,5'-hexahydroxybiphenyl (5,5'-BTO dimer) was identified.

KEYWORDS: Biobased chemicals, HMF, Benzenetriol, Lewis acids, Super critical water, Cyclohexanone, Hydrodeoxygenation



INTRODUCTION

Due to the depletion of fossil-based feedstocks and the environmental concerns related to their use, the production of chemicals from renewable resources is of major importance for achieving a sustainable chemical industry. Aromatic compounds play an important role in the chemical industry, relying mostly on oil derived benzene-toluene-xylenes (BTX).^{1,2} For example, benzene is used to produce phenol and bisphenol A as well as KA oil via cyclohexane, which are two processes important for industrial polymeric products such as nylons (Scheme 1). Biomass is an abundant and globally distributed renewable carbon resource suitable for the production of chemicals. Despite recent progress exemplified by the production of aromatics from lignin or routes from carbohydrate sources to *p*-xylene and mixtures of BTX, the production of aromatic chemicals from biomass is still a challenge.^{1–12}

5-Hydroxymethylfurfural (HMF) is a renewable platform chemical that can readily be obtained from natural carbohydrate sources and can be transformed into biofuels and valuable biobased chemicals such as 2,5-furandimethanol (FDM), 5-methylfurfural (MF), 5-methyl-2-furanmethanol (MFM) and 2,5-dimethylfuran (DMF).^{5,12} An interesting product that is

often reported as a side-product in the production and conversion of HMF is 1,2,4-benzenetriol (BTO).^{13,14} BTO is an antioxidant and offers a suitable platform for the production of pharmaceuticals, agrochemicals and dyes.^{15,16} BTO is supposedly formed via hydrolysis of the furan ring in HMF, which is later rearranged to a hexatriene ring through an electrolytic rearrangement followed by dehydration, which seems relatively favored in aqueous processes at higher temperatures and with extended reaction times.^{13,14,17–23}

In the 1990s, the group of van Bekkum looked at the optimization of the subcritical reaction conditions for the conversion of HMF to BTO and achieved up to 25 mol % BTO yield in a continuous setup. The process was run with a 0.05 M aqueous HMF feed, temperatures between 330 and 350 °C, 280 bar pressure and residence times around 250 s.^{13,14} Higher yields were difficult to obtain due to competing reactions such as the formation of levulinic acid as well as humin formation. Additionally, BTO itself was reported to be unstable leading to unknown degradation products. Even under ambient con-

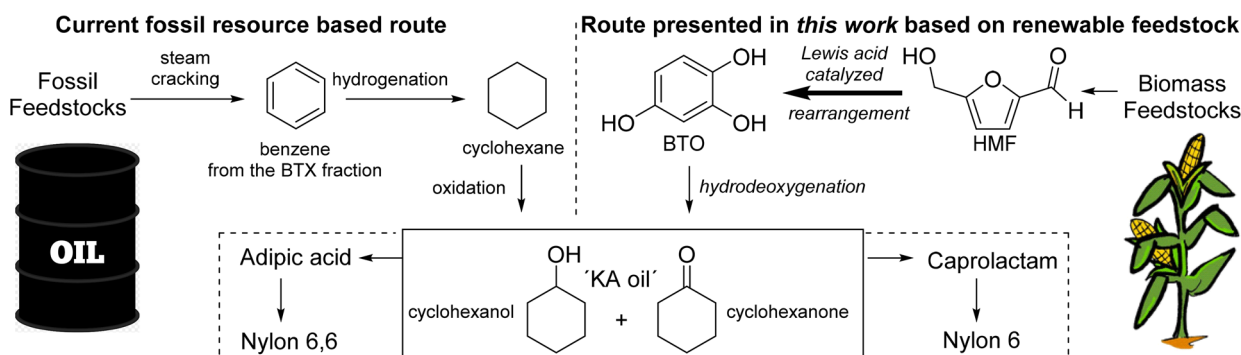
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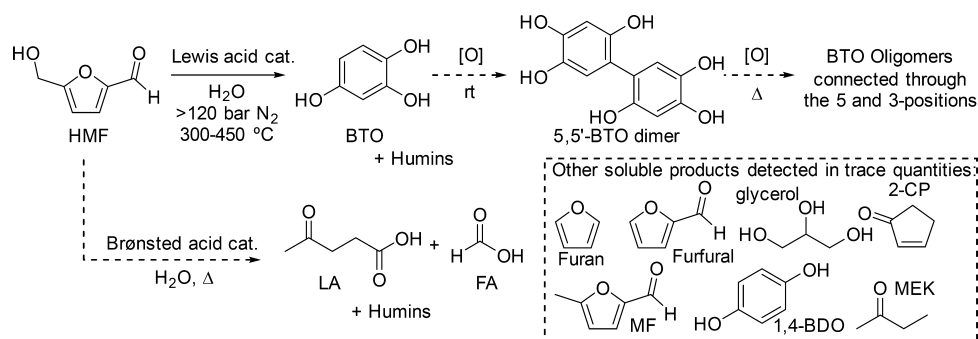
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Scheme 1. Chemical Routes toward KA Oil and Nylons, Highlighting the Route Presented in This Work Relying on Renewable Biomass Feedstocks



Scheme 2. Lewis Acid Catalyzed Conversion of HMF into BTO and Detected Side Products Formed in the Reaction Also Showing the Formation of the 5,5'-BTO Dimer and Further Oligomers



ditions, BTO slowly degrades in solution hampering accurate analysis.²³ In this work, for the first time the catalytic formation of BTO from HMF is presented as a method to significantly increase its rate of formation and selectivity. In particular, metal salts ZnCl_2 , $\text{Zn}(\text{OTf})_2$ and $\text{Fe}(\text{OTf})_2$ classified as relatively soft Lewis acids were shown to be effective. Additionally, the main degradation pathway for BTO is identified which provides insight into how this can be suppressed and appropriately corrected for in analysis. Finally, we also demonstrate the hydrodeoxygenation of BTO to cyclohexanone to provide a sustainable route to important polymeric products that avoids the use of fossil feedstocks (Scheme 1).

RESULTS AND DISCUSSION

Exploratory Reactions Including 5,5'-BTO Dimer Formation. Using a batch reactor setup heated in a fluidized sand bath, an initial screening of reaction conditions in the absence of catalyst indeed showed that 1,2,4-benzenetriol (BTO) can be obtained in significant amounts (17 mol %) from 5-hydroxymethylfurfural (HMF) at subcritical conditions ($T_{\text{bath}} = 300\text{ °C}$, P_0 120 bar N_2 , P_{final} up to 300 bar and 30–60 min reaction time).^{13,14} Under these conditions, the HMF conversion is over 95 mol % and the main product is char which is obtained as a solid at the end of the reaction. Initial exploratory catalyst screening showed that the addition of (Lewis acidic) salts such as FeCl_2 and MgCl_2 provided increased yields of BTO (up to 30 mol %). In addition to BTO, levulinic acid (LA) and formic acid (FA) were detected which are products formed through the hydration of HMF as well as some minor side products and significant amounts of char that could readily be filtered from the product mixture (Scheme 2).

In line with previous reports, we found that the analysis of BTO can be obscured due the degradation of BTO in solution.^{18,21,22} This is typically ascribed to the formation of dimers and oligomers of unknown structure, which are likely to relate to its reported air and light sensitivity.²⁴ To get more insight into the observed loss of BTO in our reaction samples, we made an effort in studying the degradation of BTO in solution (see SI section S5). We found that when exposed to air at room temperature, BTO selectively reacts with itself to form a 5,5'-C–C bonded homodimer (5,5'-BTO dimer, Scheme 2) that could be isolated as a black powder. This material was characterized by NMR and UV–vis (see SI section 5) and crystallized from water to give the molecular structure shown in Figure 1 (Figure S9 and Table S1). When a solution of BTO was heated, oligomers formed that were shown to be connected through the 3- and 5-position of BTO (Figure S10). These BTO degradation pathways could be suppressed by working

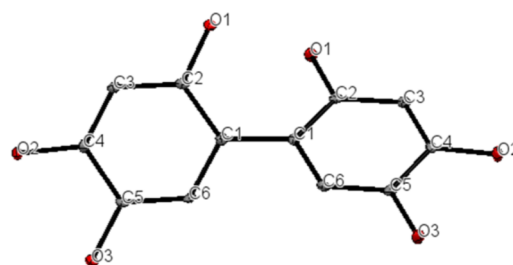


Figure 1. Molecular structure of the 5,5'-BTO dimer (2,2',4,4',5,5'-hexahydroxybiphenyl) obtained from single crystal X-ray diffraction showing 50% probability ellipsoids. Hydrogen atoms and water solvate molecules are omitted for clarity.

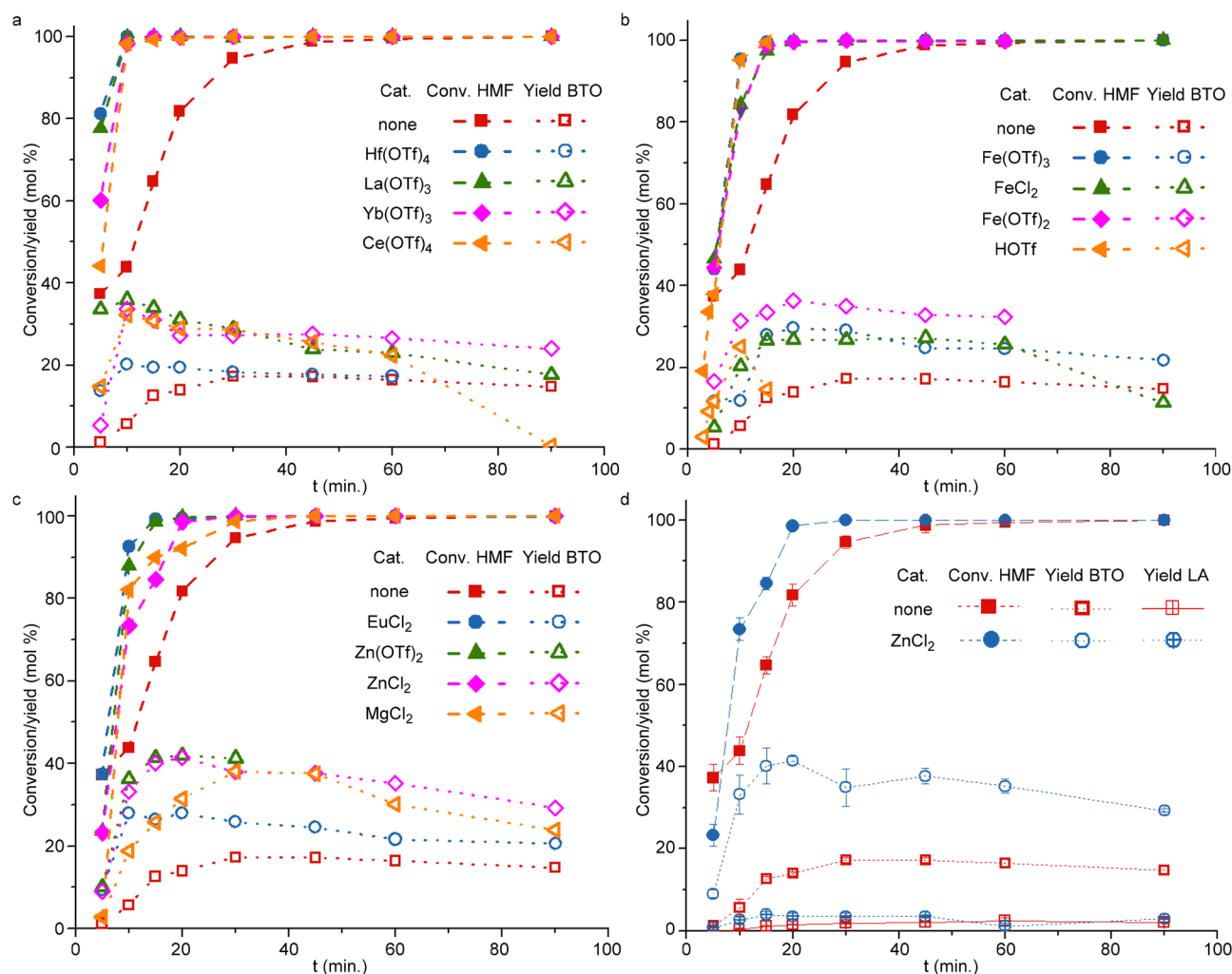


Figure 2. (a–c) Lewis acid catalyzed formation of BTO from HMF (each t data point represents a separate experiment). (d) Formation of LA and BTO from HMF with cat. ZnCl_2 and without catalyst showing average and standard deviations from 4 separate experiments. (HPLC, DMSO as internal standard. Conditions: 5 mL 0.05 M aqueous HMF and 1.2 mM cat., $T_{\text{bath}} = 300^\circ\text{C}$, $P_0 = 120$ bar N_2 .)

under oxygen-free conditions. Long-term storage of the BTO solutions could also be achieved by exclusion of air. An aqueous solution of BTO that had argon bubbled through it for 1 h and that was stored under exclusion of air showed retention of BTO and no significant 5,5'-BTO dimer formation for over 10 months (as long as the experiment was run). This observation also explains why extensive degassing of the HMF to BTO reaction solutions is essential for obtaining measurable amounts of BTO. Therefore, before each experiments in which BTO was formed from HMF, the reactor was flushed with three times 120 bar of nitrogen. Even though this prevented dimerization of the formed BTO in the reactor some 5,5'-BTO dimer was still observed upon HPLC analysis (up to 10 mol %). This is likely caused by the formation of 5,5'-BTO dimer during the sample preparation for HPLC analysis, which was not performed under exclusion of air. For this reason, we quantified the amount of 5,5'-BTO dimer by HPLC analysis and subsequently corrected the BTO yield accordingly (see SI section S3).

Lewis Acid Catalyzed Formation of BTO at Subcritical Conditions. Following the successful application of FeCl_2 and MgCl_2 in our first screening, a wider range of Lewis acid metal salt catalysts were applied to study the reaction in more detail. This was done by following the progress in time by a set of batch reactions at subcritical conditions ($T_{\text{bath}} = 300^\circ\text{C}$, >120

bar) and different reaction times by addition of 1.2 mM (2.4 mol %) Lewis acid catalyst (Figure 2a–c).

Figure 2d shows the error of a set of quadruplicate experiments for the reaction using ZnCl_2 and the noncatalyzed reactions to demonstrate the reproducibility of the experiments. The rate of HMF conversion is clearly enhanced by all metal salts showing full conversion within 10 min for several catalysts, whereas the reaction without catalyst takes about 40 min to reach full conversion. Overall, the HMF conversion rate showed the following order in increase for this set of metal salts: $\text{Hf}(\text{OTf})_4 \approx \text{La}(\text{OTf})_3 > \text{Yb}(\text{OTf})_3 > \text{Ce}(\text{OTf})_4 \approx \text{Fe}(\text{OTf})_3 \approx \text{FeCl}_2 \approx \text{Fe}(\text{OTf})_2 \approx \text{HOTf} \approx \text{EuCl}_2 \approx \text{Zn}(\text{OTf})_2 > \text{ZnCl}_2 \approx \text{MgCl}_2$.

Additionally, the selectivity for BTO increased for all applied catalysts when compared the reaction without catalyst. However, the maximum yields obtained and the reaction time at which this is achieved is markedly different. The maximum yields were increased to over 20 mol % for all catalysts and just over 40% for $\text{Zn}(\text{OTf})_2$ and ZnCl_2 (compared to 15 mol % maximum yield of BTO for the reaction without catalyst). Whereas for the reaction without catalyst the maximum yield of BTO is achieved after 30 min, most of the catalyzed reactions achieved their highest yield within 20 min. An exception was when MgCl_2 was used, which provided a reaction progress

similar to that of the reaction without catalyst nevertheless achieving a maximum BTO yield of 38 mol %. BTO appeared to be a relatively stable product under these reaction conditions as it only slowly reacted away with extended reaction times.

In order to compare the performance of the different catalysts, the reaction progress after 20 min is plotted in Figure 3 in order of the hydrolysis constants (pK_h) of the different

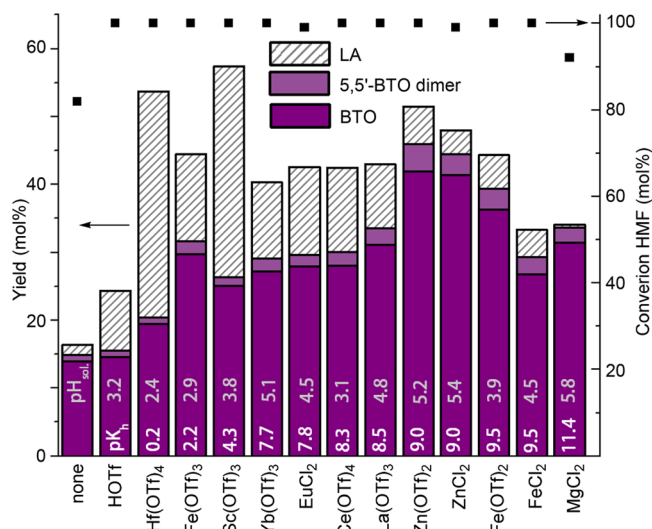


Figure 3. Lewis acid catalyzed formation of BTO from HMF as well as yields of levulinic acid (LA) and comparison to the results to the reported pK_h of the Lewis acids and the measured pH of the initial catalyst solutions. (HPLC, DMSO as internal standard. Conditions: 5 mL 0.05 M aqueous HMF and 1.2 mM cat., $T_{\text{bath}} = 300\text{ }^{\circ}\text{C}$, $P_0 = 120$ bar N_2 , $t = 20$ min.)

metal ions at $25\text{ }^{\circ}\text{C}$ ²⁵ and also showing the acidity of the solutions before reaction. Both these parameters do not show a strong correlation. Several metal salts produce lower amounts of BTO and increased amounts of levulinic acid (LA) and formic acid (FA). The formation of LA and FA from HMF is known to be acids catalyzed,²² and therefore the hydrolysis of the metal ions releasing H^+ can have an influence on the reaction outcome. However, the correlation to the pH of the catalysts is not conclusive. The pK_h and solution acidity gave only a minor indication that indeed a more acidic media leads to more LA and FA formation, whereas lower acidity leads to more selective BTO formation. The lack of definite correlations is likely caused by the presence of competing reactions toward insoluble humins that were found as major side product. BTO has been previously suggested as a humin cross-linker²⁶ and thus its formation might coincide with different rates of humin formation. Acids are known to promote the formation of humins from HMF, which is the major product obtained in the reaction without catalyst or when triflic acid is added to the reaction. The Lewis acidic metal salts that gave the highest BTO yield (Fe and Zn) are classified as relatively soft Lewis acids compared to the others used in these reactions indicating that polarizability of the charged species might also play a role.^{27,28} The use of triflate salts resulted in slightly higher BTO yields compared to chlorine salts indicating some additional influence of the counterion.

Further Optimization of the Reaction Conditions.

Experiments were performed for further optimization of the reaction conditions. For these experiments, $\text{Zn}(\text{OTf})_2$ and ZnCl_2 were selected as best performing catalysts achieving the

highest yields of BTO under the reaction conditions used for catalyst screening. Of these two catalysts, ZnCl_2 is the cheaper option but can lead to significant corrosion of metal surfaces exposed to the reaction medium and therefore has to be handled with care. First, the sand bath temperature was varied from 300 to $450\text{ }^{\circ}\text{C}$ (Figure 4). As expected, the HMF

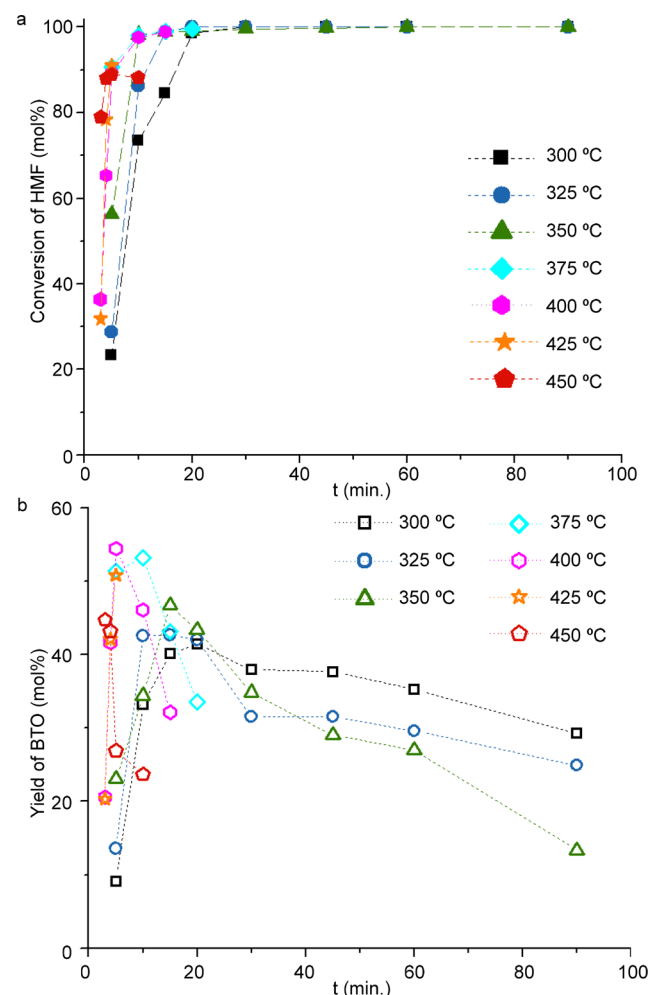


Figure 4. Reaction progress of the ZnCl_2 catalyzed formation of BTO from HMF at different sand bath temperatures (each t data point represents a separate experiment). (a) Conversion of HMF and (b) BTO yield. (HPLC, DMSO as internal standard. Conditions: 5 mL 0.05 M aqueous HMF and 1.2 mM ZnCl_2 , $P_0 = 80\text{--}120$ bar N_2 depending on the final temperature.)

conversion rate increases with the increase of temperature. At higher temperature conversion rapidly increases, but seems to level off. For example, at $450\text{ }^{\circ}\text{C}$ after 10 min the HMF conversion is the same as that observed after 5 min (around 90%). This could be due to the liquid reaching a super critical state, which would for pure water be achieved at around $375\text{ }^{\circ}\text{C}$. At the heating rate of the reactor, this temperature should be reached at around 6–7 min (see SI). A similar decrease in conversion was observed at fluidized sand bath temperatures above $375\text{ }^{\circ}\text{C}$ in which no catalyst was added (Figure S12). This could be due to a change in the polarity of water heated above the critical point possibly even causing precipitation. This could indicate that the conversion of HMF is rapid under reaction conditions but does not proceed further once the critical point is reached. As for HMF conversion, the BTO yield

increases with increasing temperature and seems to reach an optimum around 425 °C where a yield of 55% is reached for ZnCl_2 as catalysts at 89 mol % HMF conversion and 3 min reaction time, respectively. Given the measured heating rate of the liquid inside the reactor, supercritical conditions have not yet been achieved at these short reaction times. This indicates that selectivity toward BTO is highest below the super critical point. Very similar results were obtained for $\text{Zn}(\text{OTf})_2$ (Figure S11). At elevated temperatures, the BTO yield sharply decreased in time indicating that it is not a stable product under these conditions and the reaction time has to be carefully tuned to obtain the maximum yields.

In addition to the strange effect of super critical conditions on the HMF conversion, product selectivity seems to switch toward furan at elevated temperature (up to 22 mol %, see Table S2). Also, in reactions without catalyst furan becomes the major product. Additionally, when HMF was thermally converted in the absence of a solvent furan is the major reaction product (Figure S13). Next, the ZnCl_2 concentration was varied between 0.14 and 10 mM (0.28–20 mol %) at a 400 °C sand bath temperature (Figure 5). Only a slight increase in the rate of HMF conversion can be observed, but even with a

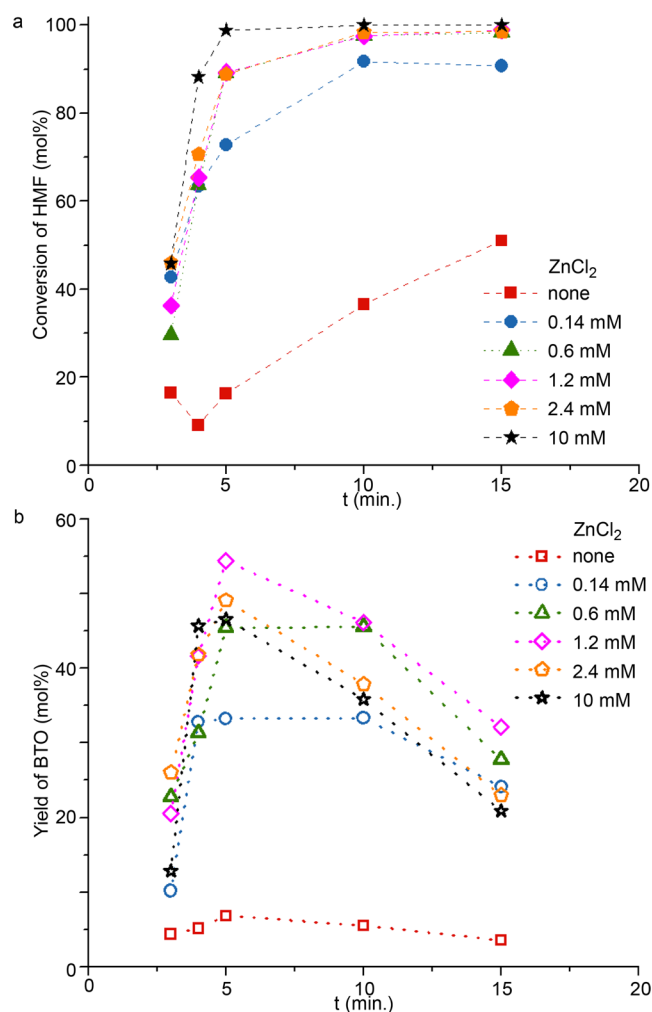
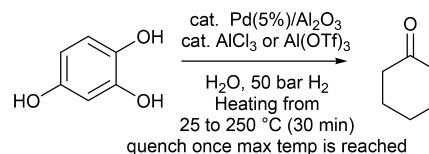


Figure 5. Reaction progress of the ZnCl_2 catalyzed formation of BTO from HMF at different catalyst concentrations (each t data point represents a separate experiment). (a) Conversion of HMF and (b) BTO yield. (HPLC, DMSO as internal standard. Conditions; 5 mL 0.05 M aqueous HMF, $T_{\text{bath}} = 400$ °C, $P_0 = 70$ –110 bar N_2 .)

small amount of catalyst a dramatic effect can be observed in the yield of BTO compared to a reaction without catalyst (7 vs 33 mol % after a 5 min reaction using 0 or 0.14 mM ZnCl_2 respectively). The BTO selectivity reaches a maximum at 1.2 mM, and with higher catalyst concentrations the maximum yield of BTO seems to plateau around 50 mol %. The use of an increased catalyst concentration leads to the formation of more 2-cyclopenten-1-one and methylfurfural (2-CP and MF, Scheme 2, Table S2). Similar observations were made when the HMF concentration was decreased (Figures S14 and S15). However, when the HMF concentration was increased to 0.1 and 0.25 M the selectivity for BTO dropped to around 10%, which is likely caused by excessive char/humin formation, which is consistent with earlier reports.^{22,23} Additionally, increased amounts of furan, furfural and methylfurfural are observed. Overall, in the setup used, the maximum yield of BTO was around 55 mol % using $\text{Zn}(\text{OTf})_2$ or ZnCl_2 as catalyst at $T_{\text{bath}} = 400$ –425 °C, 80 bar initial N_2 pressure, 5 mL 0.05 M aqueous HMF and a reaction time of around 5 min.

Catalytic Hydrodeoxygenation of BTO. BTO offers many possibilities for further derivatization that will be explored in the future. For short-term applications, the conversion to “drop-in” chemicals is more interesting.²⁹ Therefore, the catalytic hydrodeoxygenation of BTO to cyclohexanone was attempted. A mixture of cyclohexanone and cyclohexanol is also known as KA oil, an industrial relevant intermediate in the production of nylons (Scheme 1). For this purpose, a mixture of 2.5 mmol BTO in 25 mL with 0.1 g $\text{Pd}/\text{Al}_2\text{O}_3$ (5 wt %) and 0.1 g AlCl_3 as catalysts was water pressurized to 50 bar H_2 and subsequently heated until the reactor reached a temperature of 250 °C followed by rapid cooling (Scheme 3). Up to 45 mol %

Scheme 3. Catalytic Hydrodeoxygenation of BTO to Cyclohexanone in Water



yield of cyclohexanone (major product) could be achieved this way. AlCl_3 is known to be quite corrosive under the used reaction conditions. Therefore, $\text{Al}(\text{OTf})_3$ was applied as a less corrosive alternative. At exactly the same conditions $\text{Al}(\text{OTf})_3$ led to somewhat lower cyclohexanone yield (36%).

The used catalyst system is inspired by a reported procedure for the catalytic hydrogenation of phenol.³⁰ Here, AlCl_3 is shown to act as Lewis acid to activate the palladium toward ring hydrogenation and suppresses the hydrogen of cyclohexanone. This is achieved as milder conditions (50 °C, 10 bar H_2) but in a total reaction time of 7 h and in dichloromethane as solvent. Water is an excellent greener alternative solvent for hydrodeoxygenation reactions.³¹ However, in both water and dichloromethane as solvent at 50 °C, no cyclohexanone formation was observed for the catalytic hydrodeoxygenation of BTO even at extended reaction times. As mentioned, in water at increased temperature the reaction does proceed. The required increased reaction temperature is likely the result of the additional hydrodeoxygenation steps required for the conversion of BTO to cyclohexanone compared to the same reaction from phenol. In the reaction mixture also products such as 4-hydroxycyclohexanone, 1,2-cyclohexanediol (cis and

trans), 1,4-benzenediol, furan, cyclopentene, methanol, acetic acid and levulinic acid were detected. Some of the detected compounds (*cis*- and *trans*-1,2-cyclohexadiol and 4-hydroxycyclohexanone) are likely intermediates toward cyclohexanone and hexanol; however, longer reaction times did not lead to higher yield as these appeared not to be entirely stable under the reaction conditions (Figure 6 and Table S3). These

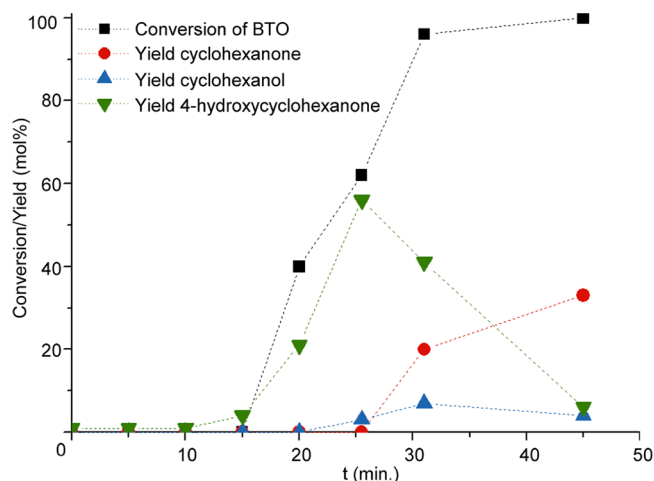


Figure 6. Hydrodeoxygenation of BTO in time using 30 wt % Pd(5%)/Al₂O₃ and 30 wt % Al(OTf)₃, 50 bar H₂, 20–250 °C (final *T* reached at 31 min, data point at 45 min is after cooling of the reactor).

reaction conditions are far from ideal, and future work is necessary to improve this reaction, likely in a different reactor setup. Nevertheless, the results show that formation of renewable cyclohexanone from BTO is possible.

CONCLUSION

This study displays the potential for the production and use of 1,2,4-benzenetriol (BTO) as a novel biobased product that can be obtained via catalytic conversion of 5-hydroxymethylfurfural (HMF). The presented procedure for the catalytic conversion of HMF to BTO relies on the use of Lewis acid catalysts that enables the production to up to 55 mol % BTO from HMF in water at (sub)supercritical conditions. In particular, metal salts classified as relatively soft Lewis acids (ZnCl₂, Zn(OTf)₂ and Fe(OTf)₂) appeared to be suitable catalysts showing significant improvement compared to the uncatalyzed reaction which yields (around 40 mol % instead of 15 mol % at 300 °C). Major side reactions are the conversion of HMF into levulinic acid and formic acid instead as well as humins, which are well-known to be acid catalyzed. Highest yields were obtained at reaction conditions close to supercritical conditions (*T*_{bath} 400 °C, 280 bar, 5 min). In addition, a BTO dimerization pathway as well as oligomerization was described which could lead to undesired product formation if not appropriately addressed. It was shown that these reactions can be suppressed by exclusion of air. Additionally, selective dimerization can be performed under controlled conditions leading to the isolation of 2,2',4,4',5,5'-hexahydroxybiphenyl (5,5'-BTO dimer), a compound that also has potential for use as starting material for other biobased products. Other products that can be obtained from BTO and its dimer will be part of future investigations.

Among many synthetic possibilities that BTO offers, the demonstrated catalytic hydrodeoxygenation of BTO to cyclohexanone comprises a new route toward biobased nylons.³²

This offers an alternative route to other HMF to caprolactam³³ and adipic acid³⁴ that can rely on current state of the art technology for the conversion of cyclohexanone/cyclohexanol to these compounds, possibly shortening the time to market. Both reaction steps (rearrangement and hydrodeoxygenation) described can be performed in water as an ideal green solvent. Although the conversion of HMF to BTO requires relatively high temperatures and pressures, this conversion is atom efficient with a cheap catalyst system and therefore relatively easy to perform when suitable equipment is available. As BTO selectivity should be increased, future research will focus on further optimization of the reaction conditions, catalyst and in particular reactor setups. For example, implementation of a continuous flow reactor would allow for improved control over residence times, which is crucial for achieving high BTO yields and the possibility for an integrated conversion to cyclohexanone.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b03648.

Data for 5,5'-BTO dimer (CIF)

additional information on the reaction setup and the formation of dimers and oligomers from BTO and additional experimental data on HMF to BTO reactions (PDF)

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Notes

The authors declare no competing financial interest.

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